Rubber-Toughened Polypropylene Nanocomposite: Effect of Polyethylene Octene Copolymer on Mechanical Properties and Phase Morphology

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ABSTRACT: Rubber-toughened polypropylene (PP)/org-Montmorillonite (org-MMT) nanocomposite with polyethylene octene (POE) copolymer were compounded in a twin-screw extruder at 230°C and injection-molded. The POE used had 25 wt % 1-octene content and the weight fraction of POE in the blend was varied in the range of 0–20 wt %. X-ray diffraction analysis (XRD) revealed that an intercalation org-MMT silicate layer structure was formed in rubber-toughened polypropylene nanocomposites (RTPPNC). Izod impact measurements indicated that the addition of POE led to a significant improvement in the impact strength of the RTPPNC, from 6.2 kJ/m^2 in untoughened PP nanocomposites to 17.8 kJ/m^2 in RTPPNC containing 20 wt % POE. This shows that the POE elastomer was very effective in converting brittle PP nanocomposites into tough nanocomposites. However, the Young's modulus, tensile strength, flexural modulus, and flexural strength of the blends decreased with respect to the PP nanocomposites, as the weight fraction of POE was increased to 20 wt %. Scanning electron microscopy (SEM) was used for the investigation of the phase morphology and rubber particles size. SEM study revealed a two-phase morphology where POE, as droplets was dispersed finely and uniformly in the PP matrix. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3441–3450, 2006

Key words: polypropylene (PP); polyethylene octene (POE); nanocomposite; org-montmorillonite (org-MMT); rubber-toughened

INTRODUCTION

Development of nanocomposites is one of the latest evolutionary steps of polymer technology. Nowadays, more than 70 companies, government agencies, and academic institutions have been identified as having research and development activities related to nanocomposites.[1–3] It is hoped that nanotechnology can lead the way to better materials for many applications, from nanowires and nanodots in electronics to nanoblends and nanocomposites in automotive applications. The current interest is in the use of layered silicates as nanoscopic filler materials, such as montmorillonite (MMT). By modifying the surface through the use of organic surfactant molecules, high aspect-ratio platelets can be incorporated into a polymer matrix. The surface-modified layered silicates (organoclay) increase their interlayer basal spacing, thereby increasing the ease of entry of polymer and serves as a compatibilizer between the hydrophilic clays and hydrophobic polymers. Using such an organoclay, various polymer nanocomposites have been produced, including polypropylene (PP) nanocomposites,[4–9] polystyrene nanocomposites,[10,11] polyamide nanocomposites,[12–15] and others.[16–19]

Currently, study of PP/organoclay nanocomposites (PPNC) has attracted the interest of many researchers because of huge commercial opportunities in both automotive and packaging. However, PPNC is relatively difficult to produce because PP does not contain any polar group in its backbone chain, hence homogenous dispersion of the polar organoclay in nonpolar PP would not be easily realized. Kawasumi et al.[20] were the first to develop an approach to create PPNC by direct melt compounding of PP with inorganic MMT in the presence of maleic anhydride (MA) modified polypropylene (PPgMAH) oligomer as a compatibilizer. A good dispersion, and mechanical properties such as stiffness, heat distortion temperature, dimensional stability, and enhanced barrier to gas permeation, have been achieved.[8,21]

One of the major deficiencies of PP and PPNC is low impact resistance, particularly at low temperatures, due to its relatively high glass transition temperature (T_g). Blending PP with an elastomeric modifier may provide the way to improve the impact resistance of the base resin. Articles published by Liang and Li[22] and Utracki[23] have reviewed the advances in toughening mechanisms of PP/elastomer blends for the last 20 years. At present, ethylene propylene rubber (EPR)

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TABLE I
Detailed Compounding Formulation

System	PP (wt %)	Organoclay (wt %)	PPgMAH (wt %)	POE (wt %)
PP	l00	0	0	0
PP/F6/C6	88	6	6	0
PP/F6/C6/E5	83	6	6	5
PP/F6/C6/E10	78	6	6	10
PP/F6/C6/E15	73	6	6	15
PP/F6/C6/E20	68	6	6	20

and ethylene–propylene–diene monomer rubber (EPDM) are the most frequently used PP impact modifiers.

In this study, an attempt has been made to investigate the toughening of PPNC blends via incorporation of a relatively new type of impact modifier known as polyethylene octene (POE) copolymer, which was developed using metallocene catalyst by Dow Chemical Company. This new POE copolymer offers a controlled level of chain branching along the polymer backbone. The narrow composition and molecular weight distribution result in improved rheological properties, such as better shear thinning behavior, melt elasticity, and melt processability. These enhanced rheological properties, which match those of the PP improve dispersion and faster mixing in rubber-modified PP blends. This results in better stiffness and toughness balance than traditional EPDMs or EPRs.[24,25] To date, little work has been done on combination of polymer nanocomposites with rubbers as toughening agents. The aim of our research was to study the effect of POE content on mechanical and phase morphology of the rubber-toughened polypropylene nanocomposites (RTPPNC).

EXPERIMENTAL

Materials

The blends used in this work are described in Table I. PP copolymer (SM-240) supplied by Titan, Malaysia. The melt flow index (MFI) and density were 25 g/10 min (at 230°C and 2.16 kgf load) and 0.9 g/cm^3, respectively. The impact modifier, POE grade Engage 8150 was supplied by DuPont Dow Elastomers. its octene content and MFI were 25 wt % and 0.5 g/10 min, respectively. The maleated PP (PPgMAH) was Orevac CA 100 with ~1 wt % of MA produced by ATOFINA, France. The organoclay (Nanomer 1.30P) was a commercial product from Nanocor Inc., USA. It was a white powder containing MMT clay (70–75 wt %) intercalated by octadecylamine (25–30 wt %).

Compounding and test specimen preparation

Blends of PP, PPgMAH, organoclay, and POE, according to Table I, were dry blended in a tumbler mixer, and then compounded by simultaneous addition of all components to a Berstoff corotating twin-screw extruder. The barrel temperature profile adopted during compounding of all blends was 180°C at the feed section and increased to 230°C at the die head. The screw rotation speed was fixed at 50 rpm. The extruded materials were injection molded into standard tensile, flexural, and Izod impact specimens, using a JSW Model NIOOB II injection-molding machine, with a barrel temperature of 170–220°C. All test specimens were allowed to condition under ambient conditions for at least 48 h prior to testing.

Mechanical tests

Tensile and flexural tests were carried out according to ASTM D638 and ASTM D790, respectively, using an Instron 5567 Universal Testing Machine under ambient conditions. The crosshead speeds of 50 and 3 mm/min were used for tensile and flexural test, respectively. The Izod impact test was carried out on notched impact specimens using a Toyoseiki Impact Testing Machine under ambient conditions. Five specimens of each formulation were tested and the average values are reported.

X-ray diffraction

X-ray diffraction analysis (XRD) was carried out with a Siemens X-ray diffractometer so as to confirm whether PP/PPgMAH/organoclay nanocomposites were formed. The diffraction patterns were recorded with a step size of 0.02°, with 2θ varying from 1.5° to 10°. The interlayer distance of organoclay in nanocomposite was derived from the peak position (d_{001} reflection) in XRD diffractograms, according to the Bragg equation.

Phase morphology

The morphology of the blends was examined using a Philips ZL40 scanning electron microscope. The samples were cryogenically fractured in liquid nitrogen and etched in heptane at 50°C for 3 h to extract the elastomeric POE phase. The samples were coated with gold prior to examination under the electron beam. An operating voltage of 10 kV and a magnification of 500× and 1000× were used.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The XRD patterns of pristine organoclay (Nanomer 1.30P) and PP nanocomposite with different content of POE copolymer (0–20 wt %) are shown in Figures 1 and 2. X-ray parameters calculated from the (001) peaks are

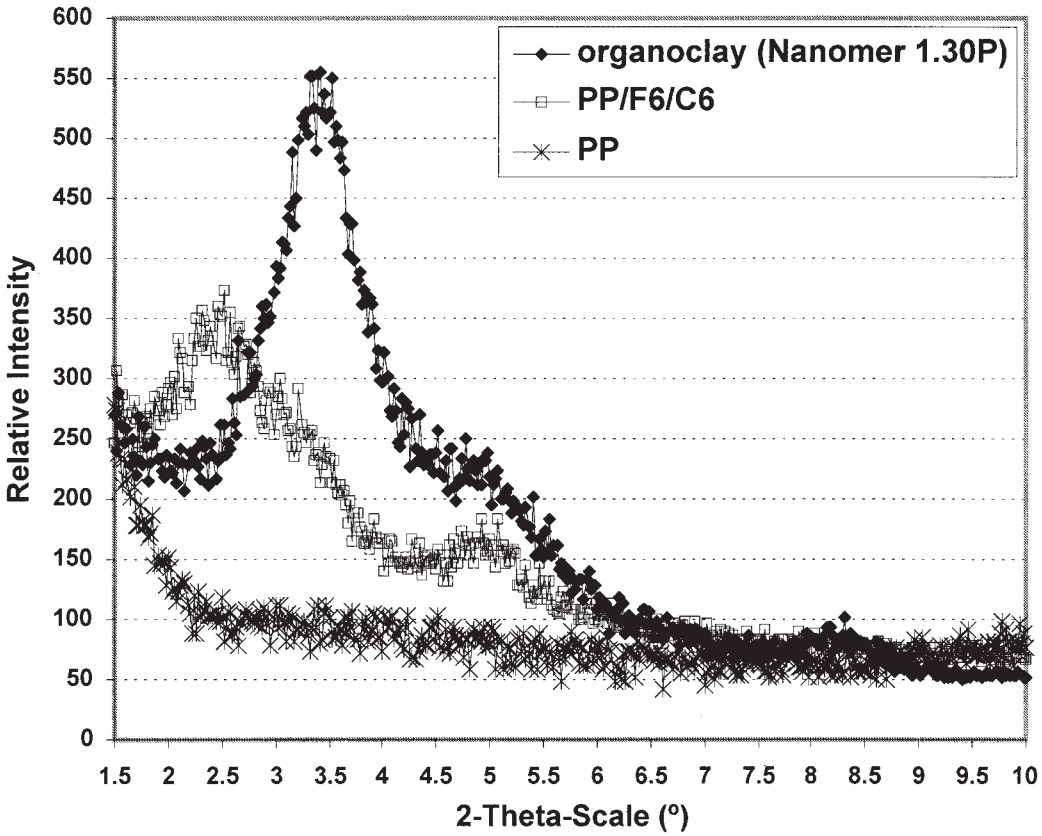


Figure 1 XRD patterns of pristine organoclay, neat PP, and PP nanocomposites.

summarized in Table II. As can be seen from Figure 1, in the PP/F6/C6 composites, the (001) organoclay plane peaks of around $2\theta = 3.40°$ were shifted to lower angles at about $2\theta = 2.46°$ comparable to that of organoclay, implying that the interlayer distance was increased from 2.60 to 3.58 nm during the direct melt blending process. This clearly indicates that the macromolecule chains had intercalated into the galleries of organoclay. The XRD pattern of PP did not show any peak in the test and therefore we used as a baseline to prove the existence of diffraction peaks due to the dispersed organoclay in the polymeric matrix.

The increasing of interlayer distance of organoclay may be the result of the strong interaction between polar PPgMAH oligomer and the silicate layer. The driving forces of the intercalation originate from the strong hydrogen bonding between MA group (COOH group generated from the hydrolysis of the MA group) and the oxygen groups of the silicates. As a result, the interlayer spacing of the clay increases and the interaction of the layers weaken. The intercalated clay with the oligomer contacts with PP under a strong shear field during extrusion process will lead macromolecule PP chains intercalated into the galleries of organoclay.[26]

Kim et al.[9] reported that, when the three components of PP, PPgMAH, and organoclay were put together and melt mixed, only PPgMAH would penetrate into the organoclay interlayer. Once the functionalized polymers are intercalated into the gallery, they constitute the long-chained surfactants. The matrix polymer can then readily penetrate into the thick interlayer and form a broad interphase, which results in the formation of intercalated/exfoliated structure.

On the other hand, with addition of 5 wt % POE copolymer into PP/F6/C6, the peak position moves toward a higher angle of about 2.78° compared with PP/F6/C6 at 2.46°, as shown in Figure 2. However, on further increase of POE copolymer concentration in PP/F6/C6, the organoclay interlayer distance remains relatively constant at about 3.30 nm. This result was quite different from the study of Li,[27] where she found that addition of styrene-ethylene propylene (SEP) rubber increased the organoclay particle dispersion, which is crucial for strengthening PP. This implies that SEP rubber has good interaction with clay particles and this interaction helps to increase clay interlayer spacing and disperse clay uniformly, but nonpolar POE copolymer had no such interaction.

Mechanical properties

The effect of adding 6 wt % organoclay and 6 wt % compatibilizer on tensile, flexural, and impact proper-

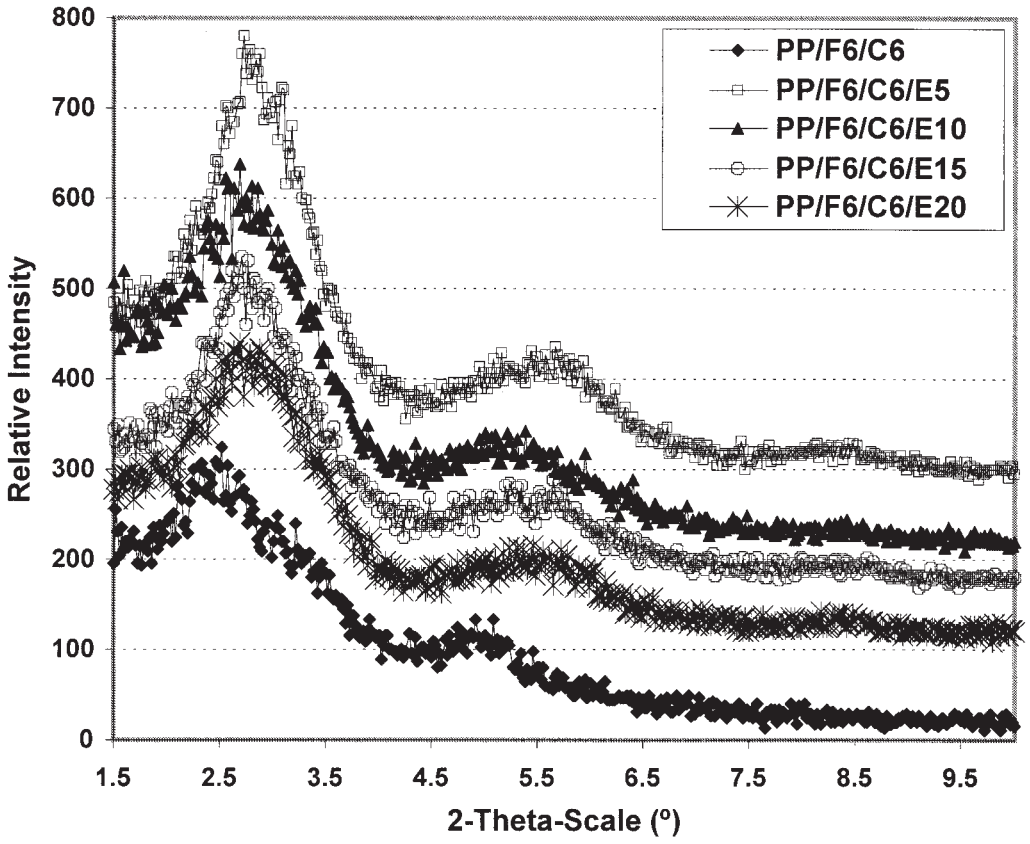


Figure 2 XRD patterns of PP nanocomposites containing POE copolymer from 0 to 20 wt %.

ties of PP were measured and are summarized in Table III. The addition of 6 wt % organoclay led to a substantial improvement in stiffness. This was indicated by the Young's modulus and flexural modulus of PP to increase by 18 and 24%, respectively. In addition, the incorporation of 6 wt % organoclay in PP blends slightly increased the flexural strength while maintaining the tensile strength. Enhancement in both modulus and strength indicated that the organoclay is able to act as reinforcing filler, because of its high aspect ratio and platelet structure.[26] This result also showed that nanoscopic organoclay filler is better than conventional micro fillers like talc and calcium carbonate, where micro filler increased composite's modulus but reduced the strength value. Manias et al.[28] reported that to obtain comparable tensile increase like the ones achieved by nanoscopic clay dispersion, 30–60 wt % of talc or mica is needed.

However, comparing PPNC to polyamide 6/polypropylene nanocomposite (PA6/PPNC),[26] the related strength enhancement due to organoclay is much higher in PA6/PPNC. This can be partially explained by the lack of interfacial adhesion between nonpolar PP and polar layered silicates. As a result, it is difficult to get exfoliated and homogenous dispersion of the silicates layer in PP matrix. However, the addition of PPgMAH to the PPNC acts as a compatibilizer to mediate the polarity between the organoclay surface and PP matrix.

TABLE II
XRD Results of Pristine Organoclay, Neat PP, and PP Nanocomposites

Sample	2θ (°)	d (nm)
Organoclay (Nanomer 1.30P)	3.40	2.60
PP	No peak detected	—
PP/F6/C6	2.46	3.58
PP/F6/C6/E5	2.78	3.18
PP/F6/C6/E10	2.67	3.31
PP/F6/C6/E15	2.67	3.31
PP/F6/C6/E20	2.65	3.33

TABLE III
Mechanical Properties of Neat PP and PP Nanocomposite

	Tensile test		Flexural test		
Properties	Young's modulus (MPa)	Tensile strength (MPa)	Flexural modulus (MPa)	Flexural strength (MPa)	Impact strength (kJ/m)
PP	1,152.0	21.6	901.2	26.7	9.3
PP/F6/C6	1,414.1	21.6	1,111.8	28.9	6.2

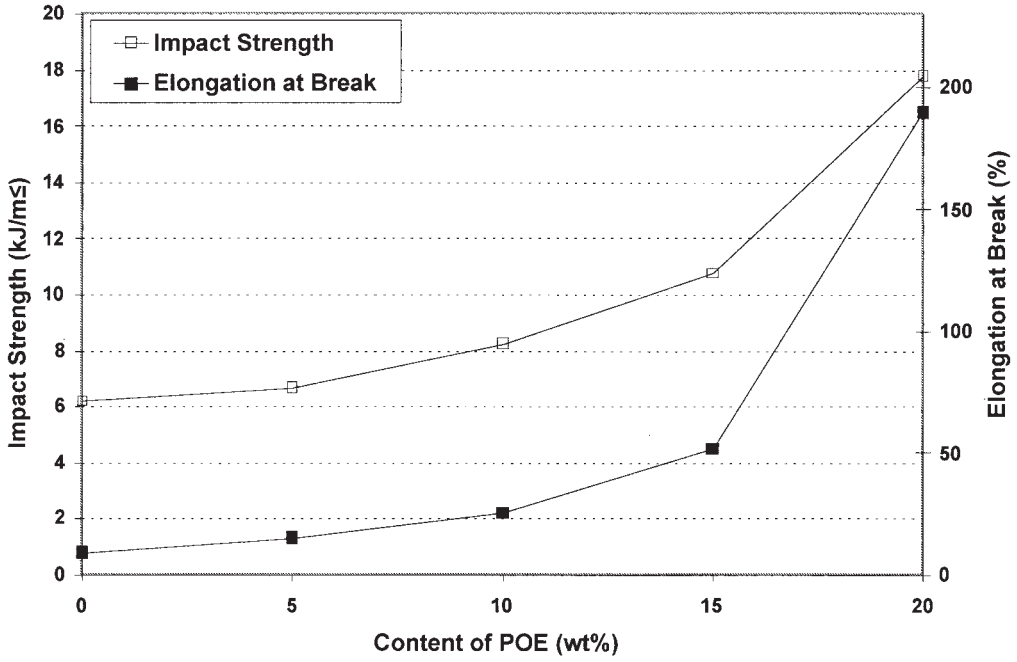


Figure 3 Effect of POE copolymer content on impact strength and elongation at break of PP nanocomposites.

This results in the nonpolar macromolecule segments of PP being able to intercalate into the interlayers of organoclay and form an intercalated PPNC. This explains the ability of PPNC to maintain the ultimate stress at an acceptable level. Hasegawa et al.[10] reported that organoclay particles dispersed more uniformly as the ratio by mass of PPgMAH to organoclay was increased. In principle, the desired nanoscale dispersion of organoclay in PP matrix is achieved with PPgMAH by strong hydrogen bonding between the hydroxl groups of the silicates and MA group, while relying on the chemical similarity of PP and grafted PP.[9]

It is also noted that the addition of 6 wt % organoclay has decreased the Izod impact strength of PP from 9.3 to 6.2 kJ/m^2. Zhang et al.[29] reported that the impact strength of PPNC decreases to less than that of pure PP, at organoclay loading of 5 wt % or more, because of the organoclay aggregates easily. A study by Garcia-Lopez et al.[30] also shows that notched Izod impact strength of PP nanocomposite decreases as the content of organoclay increases. However, it is expected that this drawback can be overcome by the incorporation of rubber phase as an impact modifier in the system. Therefore, the subsequent steps of our research have been directed toward improving the toughness-to-stiffness balance in PPNC by incorporation of POE as an impact modifier.

The effects of incorporating POE copolymer on impact strength and elongation at break of PPNC are shown in Figure 3. The results from our study revealed that the incorporation of POE copolymer phase has substantially improved the toughness and elongation at break of PP matrix. The impact strength of PPNC increased from 6.2 to 17.8 kJ/m^2, which is around a 190% increase with the addition of 20 wt % POE copolymer. This is similar to the results of Premphet and Paecharoenchai,[31] which showed that the incorporation 10% POE copolymer into neat PP matrix led to a significant improvement in impact strength.

The effectiveness of POE elastomer in toughening of PP is due to the high compatibility of a PP/POE blend. According to the studies of Carriere and Silvis,[32] the increase in the length of side chain of polyolefin elastomer from ethylene-propylene to ethylene-octene causes a significant drop in the measured interfacial tension value. This result indicates that blends of PP with ethylene-octene are more compatible than other polyolefin elastomers such as ethylene-butene or ethylene-propylene. In addition, the presence of ethylene phase in PP copolymer used in this study may further improve the compatibility between POE and PP.[33]

The increase in impact strength is, however, at the expense of tensile and flexural properties. The tensile and flexural properties of RTPPNC, given in Figures 4 and 5, show that the Young's modulus, tensile strength, flexural modulus, and flexural strength decrease almost linearly with increasing rubber content. These observations are generally found in various blends and have been reported to be due to the softening or diluting effect of the incorporation of a soft elastomeric phase to the matrix.

Scanning electron microscopy

Scanning electron microscope (SEM) was used to examine the morphology of the blends so as to

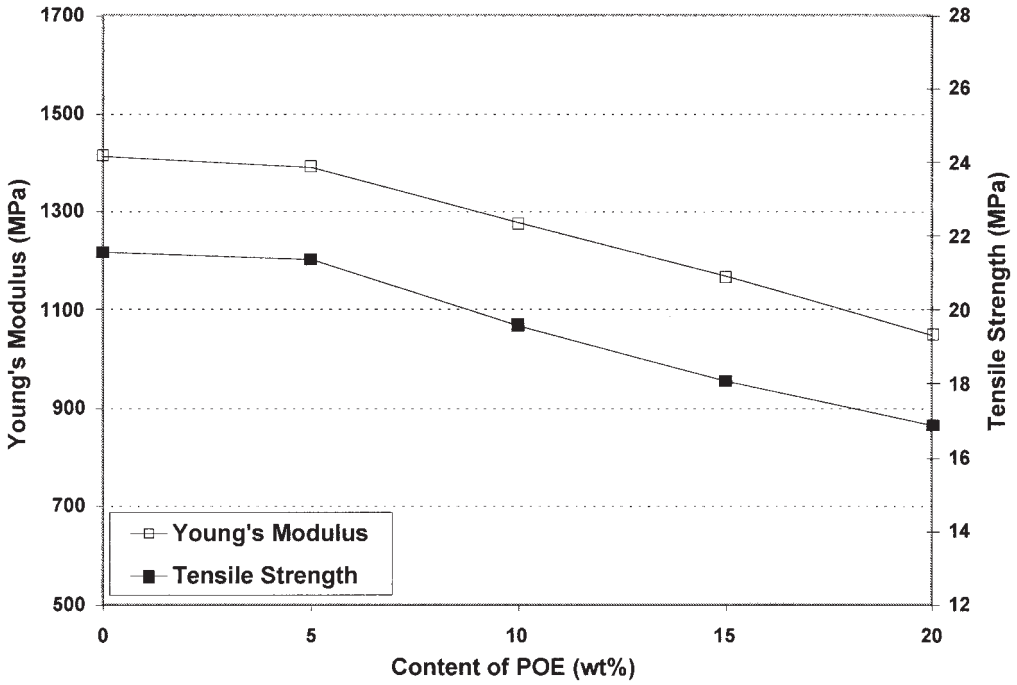


Figure 4 Effect of POE copolymer content on tensile strength and Young's modulus of PP nanocomposites.

investigate the particle size and the dispersion of POE phase in the blends system. Figures 6–8 show the phase morphology of RTPPNC blends containing 5, 10, and 20 wt % POE copolymer, respectively. The voids observed on the fracture surface are believed to be due to the removal of POE domains. The SEM photomicrographs show that a two-phase morphology is clearly visible for all systems and the droplets of POE are dispersed randomly and uniformly within the blends. The dispersed POE plays a crucial role in improving the impact strength.

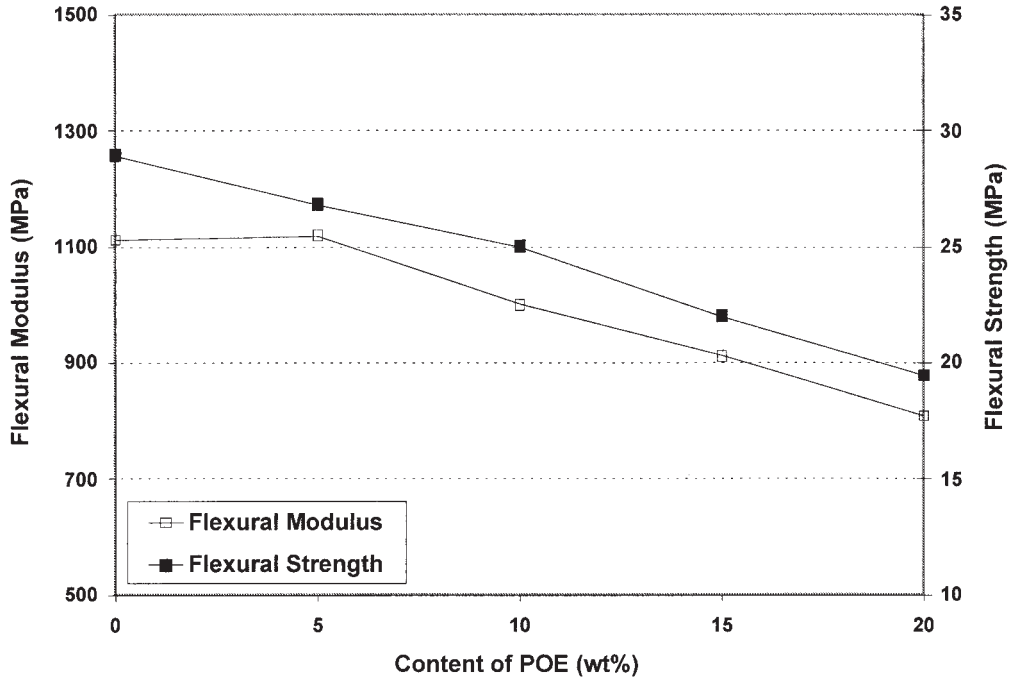
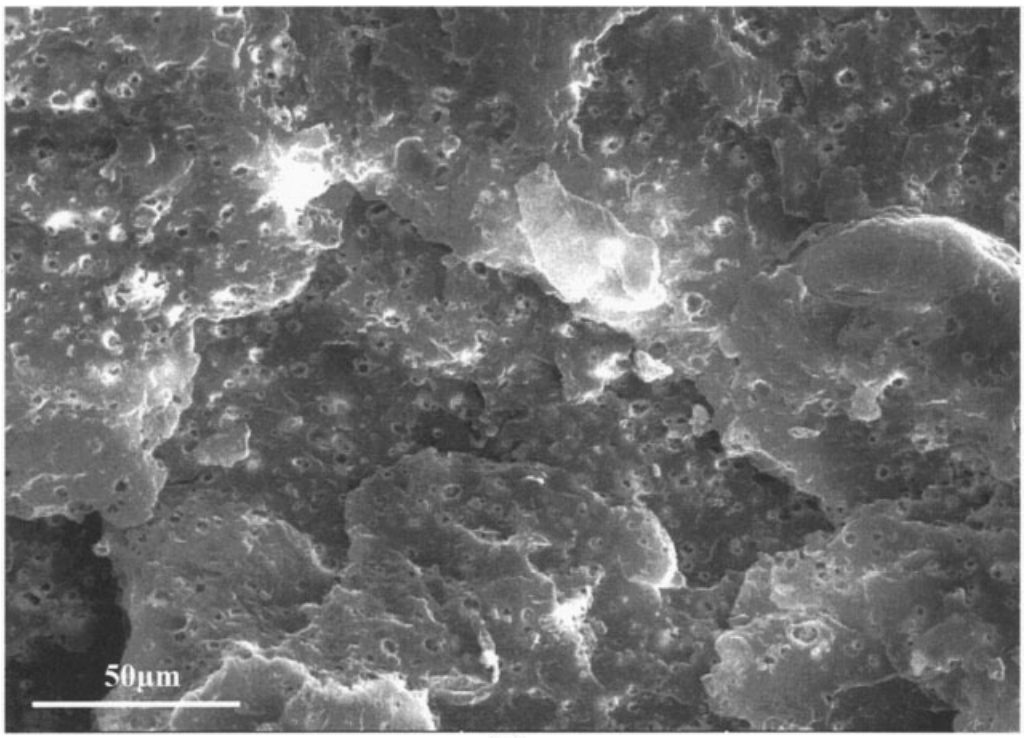
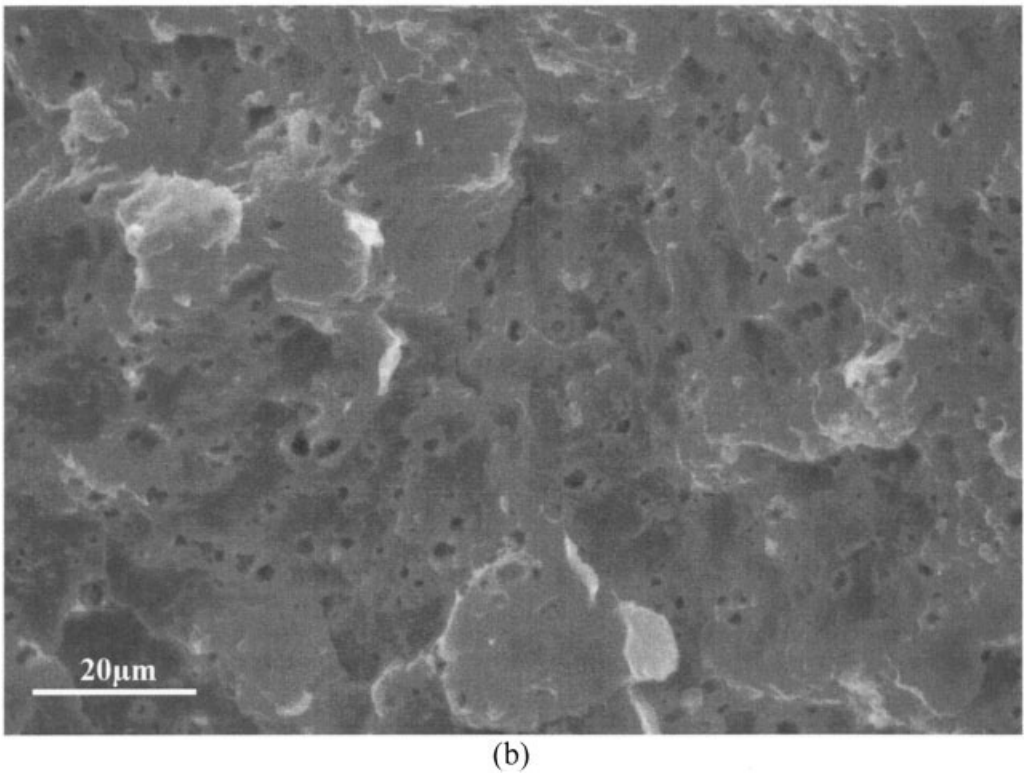


Figure 5 Effect of POE copolymer content on flexural strength and flexural modulus of PP nanocomposites.



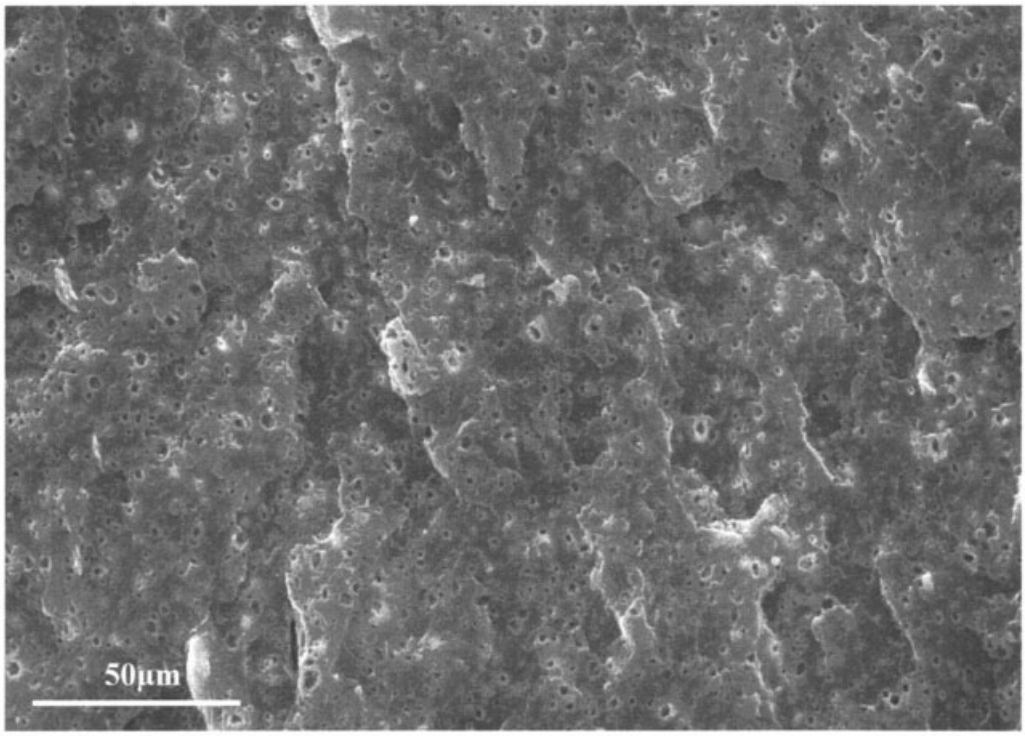
(a)



(b)

Figure 6 SEM micrograph of the cyro-fractured PP/F6/C6/E5 extracted by heptane. (a) ×500 magnification, (b) ×1000 magnification.

The amount of discrete rubber particles evidently increases with increasing rubber concentration. Visual inspection of SEM micrographs suggested that the size and shape of the dispersed particles are similar in the blends containing 5 and 10 wt % POE copolymer. A further increase in rubber content to 20 wt % contrib-



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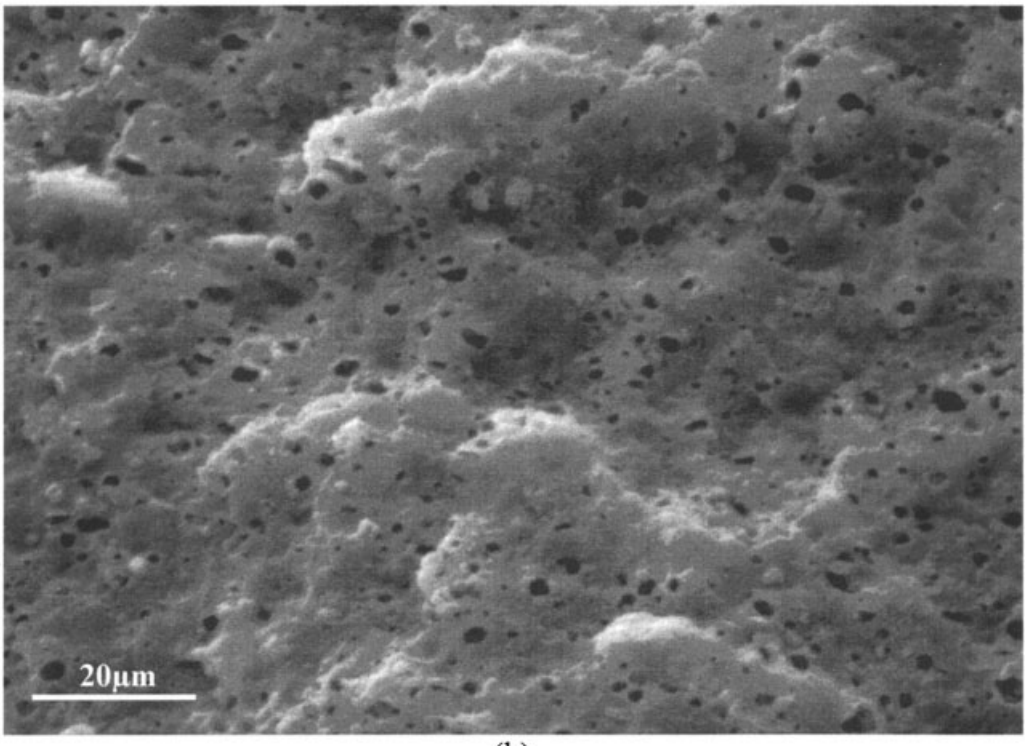

(b)

Figure 7 SEM micrograph of the cyro-fractured PP/F6/C6/E10 extracted by heptane. (a) ×500 magnification, (b) ×1000 magnification.

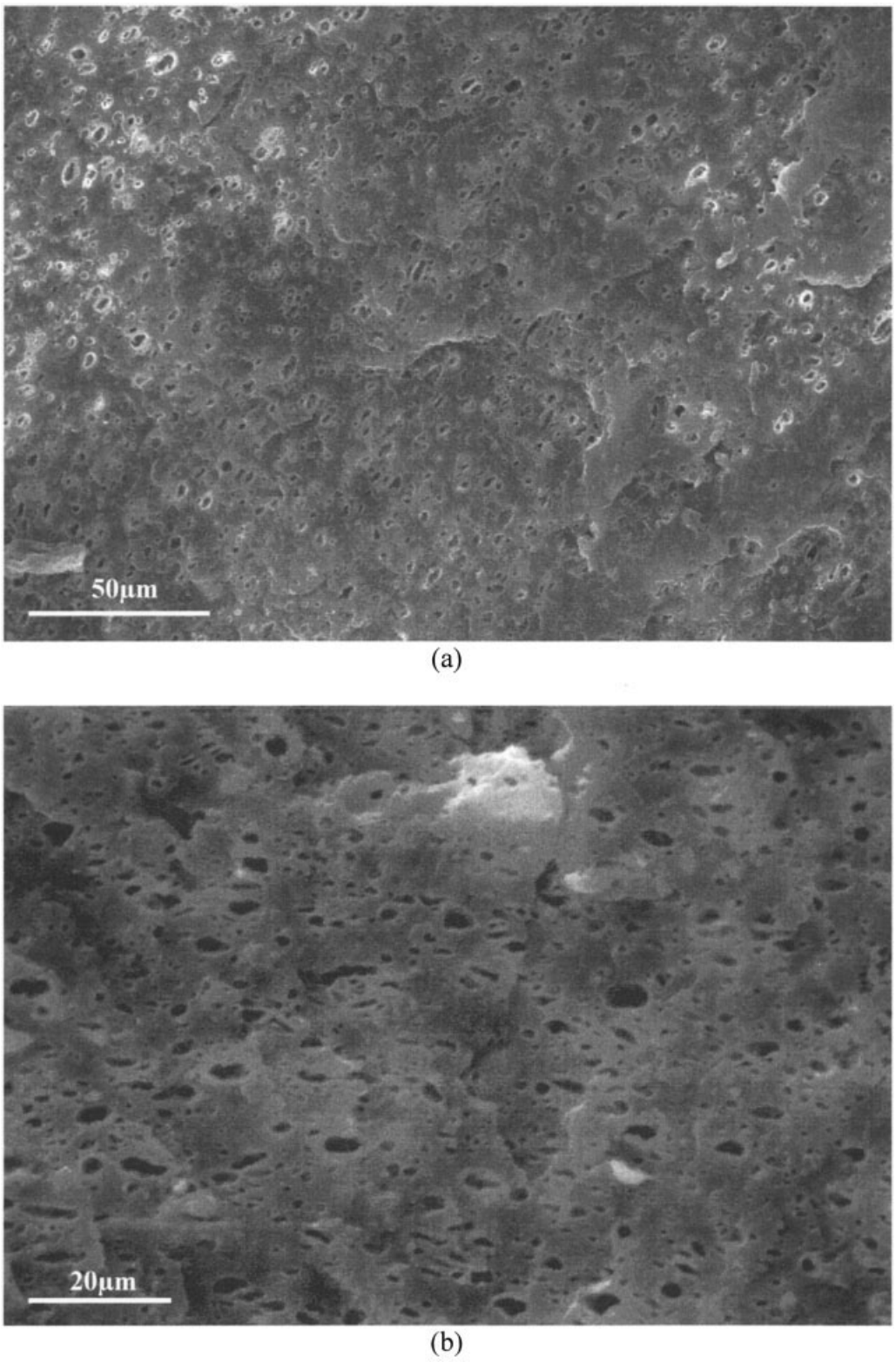

Figure 8 SEM micrograph of the cyro-fractured PP/F6/C6/E20 extracted by heptane. (a) ×500 magnification, (b) ×1000 magnification.

utes to an increase in average particle sizes and the dispersed phase had transformed from a spherical-like domain to a more elongated feature caused by the presence of populations of larger sizes in the system [Fig. 8(b)]. These results are similar to the studies of McNally et al.[34] and Premphet et al.,[35] where the

distribution of rubber particles size seems to become broader and elongated as the concentration of POE in the blends is more than 20 wt %.

CONCLUSIONS

Blends of PP, organoclay, and POE with PPgMAH as compatibilizer were successfully prepared using a twin-screw extruder. XRD analysis shows that intercalated RTPPNC have been successfully produced by the direct-melt intercalation method. The particles of silicate layers were dispersed at the nanometer level in rubber-toughened PP matrix. The Young's modulus and flexural modulus of the blends significantly improved with the incorporation of 6 wt % organoclay. Conversely, Young's modulus, tensile strength, flexural modulus, and flexural strength decreased with respect to PPNC as the concentration of POE in the blends was increased to 20 wt %. However, the notched Izod impact strength drastically improved initially from 6.2 kJ/m^2 for PPNC to 17.8 kJ/m^2 for the RTPPNC with 20 wt % POE copolymer, suggesting that POE copolymer is an efficient impact modifier for PPNC blends. This may compensate for the loss of toughness due to the addition of organoclay. The SEM study revealed a two-phase morphology wherein POE as droplets dispersed finely and uniformly in the PP matrix. A further increase in rubber content contributed to an increase in average particle sizes and transformation from a spherical like domain to a more elongated feature.

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